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**(54) PROCESS FOR PRODUCING FINE METAL OXIDE PARTICLES**

(57) This invention is a method for producing fine particles of metal oxide characterized in that metal halide is hydrolyzed in the presence of organic solvent. According to this invention, under hydrolysis of titanium tetrachloride, anatase type titanium oxide can be obtained by selecting hydrophilic organic solvent, and rutile type titanium oxide can be obtained by selecting hydrophobic organic solvent.

## Description

## TECHNICAL FIELD

[0001] This invention relates to a method for producing fine particles of metal oxide, and more specifically, relates to a method for fine particles of metal oxide with the feature of having narrower particle size distribution and moreover for the particles with a little of aggregation. Titanium dioxide (herein after as titanium oxide) is preferred as the metal oxide.

## BACKGROUND ART

[0002] In late years, in the field of fine particle forming such as ceramic, fine particles of metal oxide having narrower particle size distribution and only a little of aggregation thereof is desired as high dimension accuracy material capable of micro-working. Particularly, titanium oxide attracts attention as useful fine particle material in the field of photocatalyst, optical communication, cosmetics and so forth.

[0003] Typical crystal types of titanium oxide are rutile type and anatase type.

[0004] It is known that rutile type titanium oxide has not only excellent optical properties such as an ultraviolet light shielding property and a high refractive index, and excellent electrical properties such as an insulating property and a high dielectric property, but also excellent adsorption properties for basic antibiotic substances and uranyl carbonate in sea water.

[0005] It is known that anatase type titanium oxide has, as its strong photocatalytic action, an antibacterial action for microorganisms and the like, and its antibacterial action is effective for O-157 and MRSA (methicillin-resistant *Staphylococcus aureus*). Further, anatase type titanium oxide is applied on lighting and the like to use it as a stain-proofing agent for lighting and the like, since anatase type titanium oxide has the catalytic action.

[0006] With regard to electrical properties, rutile type one which is stable at a high temperature is more excellent in comparison with anatase type one which is easily generated at a low temperature.

[0007] It is known that rutile type one has a higher refractive index and a higher adsorption property in comparison with those of anatase type one. On the other hand, it is known that anatase type one has a higher photocatalytic activity in comparison with that of rutile type one.

[0008] Since the properties of titanium oxide are varied dependent upon its crystal type as mentioned above, it is desired to produce titanium oxides each of which has a high purity of either crystal type.

[0009] It is known that noncrystalline titanium oxide usually becomes anatase type one at 300°C, and rutile type one at 600°C, and thus, its crystal type is controlled by heating at a high temperature.

[0010] As a method for producing fine particles of metal oxide, a method for producing them by hydrolysis of metal alkoxide with organic solvent is proposed in, for example, the Japanese Patent Application Laid-Open Gazette No. Sho 61-266308 in which antimony is used as metal. A method for producing them by hydrolysis of organometal compound is proposed in the Japanese Patent Application Laid-Open Gazette No. Hei 1-230407. Various kinds of metals are listed in it.

[0011] Another method in which inorganic acid solution is added to the mixture of organic titanium compound and water-miscible organic solvent followed by hydrolysis thus producing rutile type titanium oxide is proposed (the Japanese Patent Application Laid-Open Gazette No. Hei 6-305730). However, there is a problem that the particles produced by these methods are apt to have wider particle size distribution and aggregate together.

[0012] This invention was done on the background of the above-mentioned technical problems of the prior arts, and an object of this invention is to provide a method, in which particle size is controlled easily, for producing fine particles of metal oxide, preferably titanium oxide, with the feature of having narrower particle size distribution and only a little of aggregation thereof. An another object of this invention is to provide the above described method in which where the metal oxide is titanium oxide, titanium oxide with desired crystal pattern can be produced by selection of solvent.

## DISCLOSURE OF THE INVENTION

[0013] As a result of intensive efforts to achieve the above-mentioned purposes, the present inventors accomplished this invention described below.

[0014] This invention is a method for producing fine particles of metal oxide, the method comprising a step of hydrolyzing metal halide in the presence of organic solvent to obtain the fine particles of metal oxide.

[0015] In the above-mentioned method of this invention, it is preferred that the amount of the organic solvent is from 200 to 10,000 parts by volume to 100 parts by volume of water.

[0016] It is also preferred that the mean particle size of the fine particles of metal oxide is 20nm or less than 20nm.

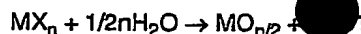
[0017] In the above-mentioned method of this invention, it is preferred that the metal halide is titanium tetrachloride and the metal oxide is titanium dioxide.

[0018] In this case, when the organic solvent may be hydrophilic and the titanium dioxide is anatase type.

[0019] Alternatively, when the organic solvent may be hydrophobic and titanium dioxide is rutile type.

[0020] According to this invention, fine particles of metal oxide with mean particle size of 20nm or less than 20nm, narrower particle size distribution and only a little of aggregation thereof can be made.

## BRIEF DESCRIPTION OF THE DRAWING



[0021]

Fig. 1 is an X-ray diffraction pattern of anatase type crystalline titanium oxide of this invention.

Fig. 2 is an X-ray diffraction pattern of rutile type crystalline titanium oxide of this invention.

## BEST MODE FOR CARRYING OUT THE INVENTION

[0022] This invention will be hereinafter explained in detail.

[0023] The method for producing fine particles of metal oxide of this invention is basically a method of hydrolysis of metal halide and this invention enables the achievement of the above-mentioned purposes by adding organic solvent, preferably in a large amount of the solvent, during the hydrolysis.

[0024] Examples of metal oxide targeted by this invention are metal oxides obtained by hydrolysis of metal halide, for example, oxides of metals categorized in the III, IV and V groups of periodic table, such as silicon oxide, germanium oxide, tin oxide, titanium oxide, zirconium oxide, boron oxide, gallium oxide, indium oxide, thallium oxide, scandium oxide, yttrium oxide, lanthanum oxide, antimony oxide, bismuth oxide, vanadium oxide, niobium oxide, tantalum oxide, lanthanoid oxide and actinoid oxide, preferably, silicon oxide, germanium oxide, titanium oxide, zirconium oxide, tin oxide and tantalum oxide, more preferably, titanium oxide.

[0025] Metal halides to be used to obtain the above-mentioned metal oxides by hydrolysis are metal halide represented by the general formula:  $MX_n$  (wherein M is metal element, X is halogen and n is integral number corresponding to the valence of M).

[0026] Example of such metal halide is, for example, silicon chloride, germanium chloride, tin chloride, titanium chloride, zirconium chloride, boron chloride, gallium chloride, indium chloride, thallium chloride, scandium chloride, yttrium chloride, lanthanum chloride, antimony chloride, bismuth chloride, vanadium chloride, niobium chloride, tantalum chloride, lanthanoid chloride, actinoid chloride, silicon bromide, germanium bromide, tin bromide, titanium bromide, zirconium bromide, boron bromide, gallium bromide, indium bromide, thallium bromide, scandium bromide, yttrium bromide, lanthanum bromide, antimony bromide, bismuth bromide, vanadium bromide, niobium bromide, tantalum bromide, lanthanoid bromide, actinoid bromide, preferably silicon chloride, germanium chloride, titanium chloride, zirconium chloride, silicon bromide, germanium bromide, titanium bromide, zirconium bromide, more preferably titanium chloride (titanium tetrachloride).

[0027] These metal halides may be used alone or in any combination of two or more thereamong.

[0028] The hydrolysis of these metal halides is represented as the following formula:

(where n of  $MX_n$  is 3 or 5,  $MO_{n/2}$  becomes  $M_2O_3$  or  $M_2O_5$ ) by using the above-mentioned general formula of  $MX_n$ .

[0029] Theoretical volume of water necessary to hydrolysis is determined by use of the above-mentioned formula.

[0030] In this invention, the amount of water is preferably from 1 to 100 times of this theoretical volume, more preferably the range of from 1 to 10 times. Where there is too much water, aggregation of fine particles produced is likely to be significant.

[0031] Water to be used in this invention may be service water, distilled water and ion-exchanged water. Among these water, distilled water or ion-exchanged water is preferable, and ion-exchanged water with electric conductivity being  $2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$  or less is more preferable.

[0032] The organic solvent to be used in this invention is any organic solvent having its freezing point less than the temperature which metal halide is not hydrolyzed with water, is preferably one having its freezing point of  $0^\circ \text{C}$  or lower, more preferably one having its freezing point of  $-10^\circ \text{C}$  or lower.

[0033] Such organic solvent includes organic solvent not able to react with metal halide, such as alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, halogenated hydrocarbons, ketones, esters, ethers, aldehydes, sulfoxides, sulfones, sulfonate esters.

[0034] Examples of such organic solvents are methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, nonanol, benzyl alcohol, methylcyclohexanol, ethanediol, propanediol, butanediol, pentanediol, hexylenediol, octylenediol, hexanetriol, butyl formate, pentyl formate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, pentyl acetate, hexyl acetate, benzyl acetate, 3-methoxybutyl acetate, 2-ethylbutyl acetate, 2-ethylhexyl acetate, methyl propionate, ethyl propionate, butyl propionate, pentyl propionate, dimethylformamide, dimethylacetamide, diethylformamide, diethylacetamide, dimethyl ketone, methyl ethyl ketone, pentanone, hexanone, methyl isobutyl ketone, heptanone, diisobutyl ketone, acetonitrile, diethyl ether, dipropyl ether, diisopropyl ether, dibutyl ether, dihexyl ether, anisole, tetrahydrofuran, tetrahydropyran, dimethoxyethane, diethoxyethane, dibutoxyethane, diethylene glycol dimethyl ether, diethylene glycol diethyl ether, ethylene glycol dibutyl ether, methylal, acetal, pentane, hexane, heptane, octane, nonane, decane, dodecane, toluene, xylene, ethylbenzene, cumene, mesitylene, tetrahydronaphthalene, butylbenzene, cymene, diethylbenzene, pentylbenzene, dipentylbenzene, cyclopentane, cyclohexane, methyl cyclohexane, ethyl cyclohexane, decalin, chloromethane, dichloromethane, trichloromethane, tetrachloromethane, chloroethane, dichloroethane, trichloroethane, tetrachloroethane, pentachloroethane, chloropropane,

dichloropropane, trichloropropane, chlorobutane, dichlorobutane, trichlorobutane, chloropentane, chlorobenzene, dichlorobenzene, chlorotoluene, dichlorotoluene, bromomethane, bromoethane, bromopropane, bromobenzene, chlorobromoethane, and so forth. Among these, alcohols, amides and hydrocarbons are preferable, and ethyl alcohol, dimethylformamide, dimethylacetamide and toluene are more preferable. The above-mentioned organic solvent may be used alone or in any combination of two or more thereamong.

[0035] A method for mixing above-mentioned metal halide, water and organic solvent is not restricted. For example, in the beginning step, water may be mixed with organic solvent, and then metal halide may be added to the resultant mixture. In this way, where water is mixed with organic solvent homogeneously, the resultant mixture can be used as it is.

[0036] Where water can not be mixed with organic solvent homogeneously, surfactant such as sodium 1,2-bis-(2-ethylhexyloxycarbonyl) -1- ethane sulfonate and polyoxyethylene alkyl phenyl ether, agitation or sonication may be used to accomplish the uniformity of the mixture. Upon using surfactant for dispersion, the composition of this invention would be usually w/o type emulsion because of high content of organic solvent.

[0037] Alternatively, in the beginning step, metal halide may be added to water, and then organic solvent may be added to the resultant mixture. In this way, it is necessary that the temperature of the mixture of water and metal halide is kept under the temperature not to occur hydrolysis before organic solvent is added. This is because it is an essential element of this invention that hydrolysis of metal halide is done in the presence of organic solvent.

[0038] The amount of water added to metal halide is preferable in the above-mentioned range, and this invention is characterized in that organic solvent, preferably a large amount of organic solvent is used with water. That is, the amount of organic solvent mixed with 100 parts by volume of water is preferably from 200 to 10,000 parts by volume, and more preferably from 1,000 to 7,000 parts by volume. Where organic solvent is too little, fine particles produced grow up with binding each other and it is apt to be difficult to control the particle size, and on the other hand, it prevents this problem effectively to add more than 200 parts by volume of organic solvent. However, where the amount of organic solvent added is more than 10,000 parts by volume, the solution is too dilute and whereby operations after producing fine particles such as centrifugation and filtration are apt to be difficult and to disadvantage the cost.

[0039] Hydrolysis is done by heating the above-mentioned mixture. While hydrolysis temperature is not particularly restricted as long as hydrolysis is proceeded, the temperature is preferably close to the boiling point of the mixture or the dispersion in a view of accelerating reaction rate.

[0040] One embodiment of the invention in which

the metal oxide is titanium oxide will be explained in detail. Under this invention in which titanium halide is hydrolyzed in the presence of organic solvent, and crystal pattern of the titanium oxide produced can be changed depending on the kind of organic solvent. That is, the produced titanium oxide is anatase type where organic solvent to be used is hydrophilic, while the produced titanium oxide is rutile type where organic solvent is hydrophobic. This enable to obtain desired crystal type of titanium oxide suitable for various kinds of applications.

[0041] The term of hydrophilic organic solvent herein means organic solvent miscible with water under the room temperature, and examples of organic solvent preferably used in this invention are alcohols such as methanol, ethanol and butanol, amides such as dimethyl acetamide and dimethyl formamide, ketones such as acetone and methyl ethyl ketone. The term of hydrophobic organic solvent herein means organic solvent non-miscible with water under the room temperature, and particularly preferable examples used in this invention are aromatic hydrocarbons such as benzene, toluene and xylene, aliphatic hydrocarbons such as hexane, heptane and octane.

[0042] Examples of titanium halide used for hydrolysis in this invention are titanium chloride such as  $TiCl_4$ , titanium bromide such as  $TiBr_4$  and titanium iodide such as  $TiI_4$ . Among these,  $TiCl_4$  is most preferable.

[0043] The other conditions, such as mixing ratio of titanium halide, water and organic solvent and hydrolysis condition are the same as the above-described ones.

[0044] Fine particles of metal oxide produced by hydrolysis are separated from the reaction mixture by use of filtration, centrifugation and so forth, washed, and then dried by use of hot-air drying, infrared drying, spray drying or vacuum drying.

[0045] Fine particles of metal oxide produced according to the above-described method have mean particle size of 20nm or smaller, and are unlikely to aggregate together during preservation, and thereby can be used as material for ceramic and other product as it is, or can be used after burning.

#### EXAMPLES

[0046] This invention will be hereinbelow explained in detail by some examples. However, this invention is not limited by the following examples.

(Example 1)

[0047] Three gram of titanium tetrachloride and 2 ml of water were added into a 100 ml-volume flask, and then 40 ml of dimethylformamide was added to them, and the flask was equipped with reflux condenser followed by heating at 100°C for 1 hour to hydrolyze the titanium tetrachloride. The resultant sol was separated

by centrifugation, and washed with ethanol, water followed by drying under reduced pressure, obtain fine particles. An X-ray diffraction analysis of the resultant fine particles showed that it was anatase type crystalline titanium oxide. The X-ray diffraction is shown as Fig. 1. An analysis by transmission electron microscope showed that the particles had 2 - 3 nm particle size and narrow particle size distribution.

(Example 2)

[0048] Three gram of titanium tetrachloride and 2 ml of water were added into a 100 ml-volume flask, and then 40 ml of ethanol was added to them, and the flask was equipped with reflux condenser followed by heat-refluxing for 1 hour to hydrolyze the titanium tetrachloride. After washing, the resultant sol was treated by the same as set forth in Example 1 to obtain fine particles (provided that washing was done only with water). An X-ray diffraction analysis of the resultant fine particles showed that it was anatase type crystalline titanium oxide. An analysis by transmission electron microscope showed that the particles had 2 - 6 nm particle size and narrow particle size distribution.

(Example 3)

[0049] Three gram of titanium tetrachloride and 2 ml of water were added into a 100 ml-volume flask, and then 40 ml of toluene was added to them, and the flask was equipped with reflux condenser followed by heating at 100°C for 1 hour to hydrolyze the titanium tetrachloride. The procedures as set forth in Example 1 were repeated to obtain fine particles. An X-ray diffraction analysis of the resultant fine particles showed that it was rutile type crystalline titanium oxide. The X-ray diffraction is shown as Fig. 2. An analysis by transmission electron microscope showed that the particles had 2-7 nm particle size and narrow particle size distribution.

(Example 4)

[0050] Titanium tetrachloride 3.7 g was dissolved in 40 ml of dimethylformamide at about 10 °C before the resultant solution was transferred into a 100 ml-volume flask. Then 0.7 ml of water was added dropwise so as not to raise the temperature followed by heating them at 100 °C for 1 hour to hydrolyze the titanium tetrachloride. The procedures as set forth in Example 1 was repeated to obtain fine particles. An X-ray diffraction analysis of the resultant fine particles showed that it was anatase type crystalline titanium oxide. An analysis by transmission electron microscope showed that the particles had 2 - 4 nm particle size and narrow particle size distribution.

(Example 5)

[0051] Three gram of silicon chloride ( $\text{SiCl}_4$ ) and 2 ml of water were added into a 100 ml-volume flask and then 40 ml of dimethylacetamide was added to them, and the flask was equipped with reflux condenser followed by heating at 100 °C for 1 hour to hydrolyze the silicon chloride. The procedures as set forth in Example 1 was repeated to obtain 1.2 g of fine particles. An x-ray diffraction analysis of the resultant fine particles showed that it was crystalline silicon oxide ( $\text{SiO}_2$ ). An analysis by transmission electron microscope showed that the particles had 3 - 5 nm particle size and narrow particle size distribution.

(Example 6)

[0052] with a 100 ml-volume flask, 5.8 g of antimony chloride ( $\text{SbCl}_3$ ) was dissolved in 40 ml of dimethylacetamide at about 10 °C, and then 0.9 ml of water was added dropwise so as not to raise the temperature. The flask was equipped with reflux condenser followed by heating at 100 °C for 1 hour to hydrolyze the antimony chloride. The procedures as set forth in Example 1 were repeated to obtain 2 g of fine particles. An X-ray diffraction analysis of the resultant fine particles showed that it was crystalline antimony oxide ( $\text{Sb}_2\text{O}_3$ ). An analysis by transmission electron microscope showed that the particles had 2 - 5 nm particle size and narrow particle size distribution.

(Example 7)

[0053] With a 100 ml-volume flask, 5.1 g of tin chloride ( $\text{SnCl}_4$ ) was dissolved in 40 ml of dimethylacetamide at about 10 °C, and then 0.7 ml of water was added dropwise so as not to raise the temperature. The flask was equipped with reflux condenser followed by heating at 100 °C for 1 hour to hydrolyze the tin chloride. The procedures as set forth in Example 1 were repeated to obtain 2.5 g of fine particles. An X-ray diffraction analysis of the resultant fine particles showed that it was crystalline tin oxide ( $\text{SnO}_2$ ). An analysis by transmission electron microscope showed that the particles had 2 - 4 nm particle size and narrow particle size distribution.

(Example 8)

[0054] With a 100 ml-volume flask, 4.5 g of zirconium chloride ( $\text{ZrCl}_4$ ) was dissolved in 40 ml of dimethylacetamide at about 10 °C, and then 0.7 ml of water was added dropwise so as not to raise the temperature. The flask was equipped with reflux condenser followed by heating at 100 °C for 1 hour to hydrolyze the zirconium chloride. The procedures as set forth in Example 1 were repeated to obtain 2.1 g of fine particles. An X-ray diffraction analysis of the resultant fine particles showed

that it was crystalline zirconium oxide ( $ZrO_2$ ). Analysis by transmission electron microscope showed that the particles had 3 - 5 nm particle size and narrow particle size distribution.

#### (Example 9)

[0055] With a 100 ml-volume flask, 7 g of tantalum chloride ( $TaCl_5$ ) was dissolved in 40 ml of dimethylacetamide at about 10 °C, and then 0.9 ml of water was added dropwise so as not to raise the temperature. The flask was equipped with reflux condenser followed by heating at 100 °C for 1 hour to hydrolyze the tantalum chloride. The procedures as set forth in Example 1 were repeated to obtain 2.5 g of fine particles. An X-ray diffraction analysis of the resultant fine particles showed that it was crystalline tantalum oxide ( $Ta_2O_5$ ). An analysis by transmission electron microscope showed that the particles had 2 - 3 nm particle size and narrow particle size distribution.

#### (Example 10)

[0056] With a 100 ml-volume flask, 4.2 g of germanium chloride ( $GeCl_4$ ) was dissolved in 40 ml of dimethylacetamide at about 10 °C, and then 0.7 ml of water was added dropwise so as not to raise the temperature. The flask was equipped with reflux condenser followed by heating at 100 °C for 1 hour to hydrolyze the germanium chloride. The procedures as set forth in Example 1 were repeated to obtain 1.8 g of fine particles. An X-ray diffraction analysis of the resultant fine particles showed that it was crystalline germanium oxide ( $GeO_2$ ). An analysis by transmission electron microscope showed that the particles had 2 - 3 nm particle size and narrow particle size distribution.

[0057] Any fine particles obtained by the above described examples has little or only a little of aggregation thereof and good dispersibility.

#### INDUSTRIAL APPLICABILITY

[0058] According to this invention, metal halide is hydrolyzed with water in the presence of organic solvent, whereby fine particles of metal oxide having only a little of aggregation thereof and good dispersibility can be obtained, where the amount of organic solvent is in the range of from 200 to 10,000 parts by volume to 100 parts by volume of water, this effect is significant. The particle size distribution also can be within considerable narrow range.

[0059] Where metal halide is titanium tetrachloride and metal oxide is titanium oxide, crystal pattern of titanium oxide can be controlled as either anatase or rutile type by selecting hydrophilic or hydrophobic organic solvent, and such type can be selected in compliance with any application, and therefore, this invention provides a method for producing fine particles capable of control-

ling crystal pattern voluntarily.

#### Claims

1. A method for producing fine particles of metal oxide, wherein said method comprising a step of hydrolyzing metal halide in the presence of organic solvent to obtain the fine particles of metal oxide.
2. A method for producing fine particles of metal oxide according to Claim 1, wherein the amount of said organic solvent is from 200 to 10,000 parts by volume to 100 parts by volume of water.
3. A method for producing fine particles of metal oxide according to Claim 1 or 2, wherein the mean particle size of said fine particles of metal oxide is 20 nm or smaller.
4. A method for producing fine particles of metal oxide according to any one of Claims 1 to 3, wherein said metal halide is titanium tetrachloride and said metal oxide is titanium dioxide.
5. A method for producing fine particles of metal oxide according to Claim 4, wherein said organic solvent is hydrophilic and said titanium dioxide is anatase type.
6. A method for producing fine particles of metal oxide according to Claim 4, wherein said organic solvent is hydrophobic and said titanium dioxide is rutile type.

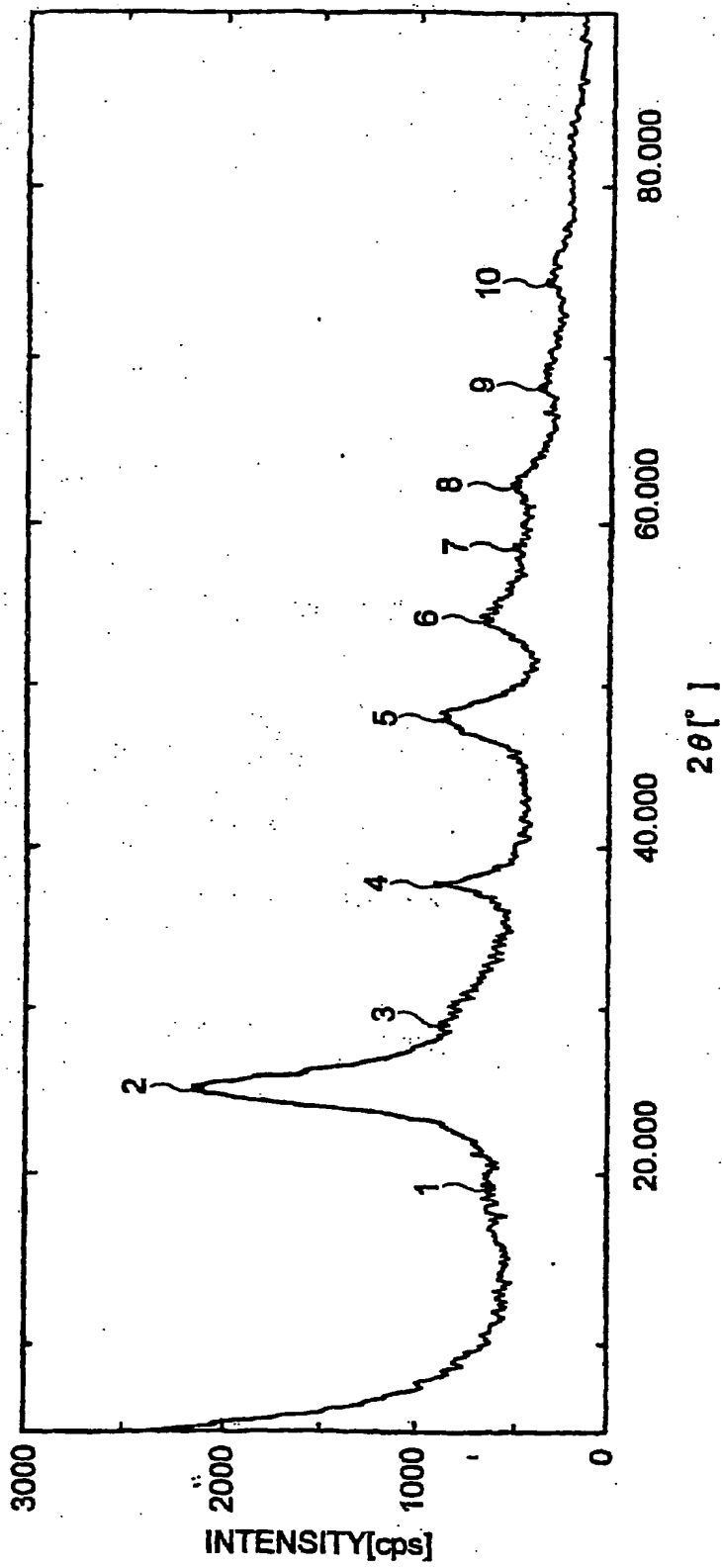
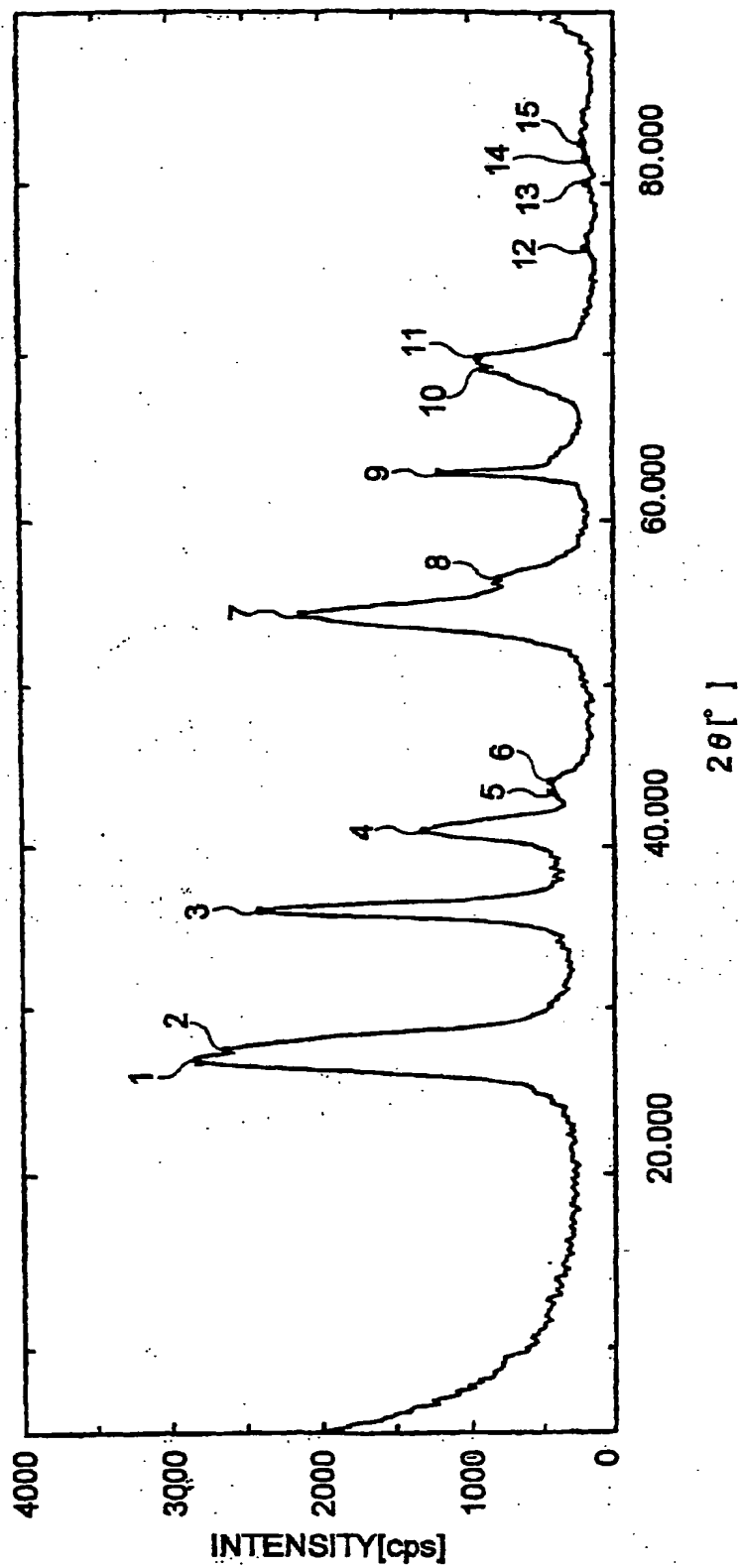
**Fig.1**

Fig.2





## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/03604

A. CLASSIFICATION OF SUBJECT MATTER  
Int.Cl<sup>5</sup> C01G23/053

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
Int.Cl<sup>5</sup> C01G1/00-57/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, 49-125299, A (Osaka Titanium Co., Ltd.), 30 November, 1974 (30. 11. 74) (Family: none)	1-6
Y	JP, 59-223231, A (Teijin Chemicals Ltd.), 15 December, 1984 (15. 12. 84) (Family: none)	1-6
A	JP, 7-223815, A (Canon Inc.), 22 August, 1995 (22. 08. 95) & EP, 674237, A & US, 5635326, A	1-6

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search  
14 December, 1998 (14. 12. 98)Date of mailing of the international search report  
15 December, 1998 (15. 12. 98)Name and mailing address of the ISA/  
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